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METHOD OF PREPARING FIBERS FROM BY-PRODUCT SLAG OF A PHOSPHORUS FURNACE

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FIG. 2.

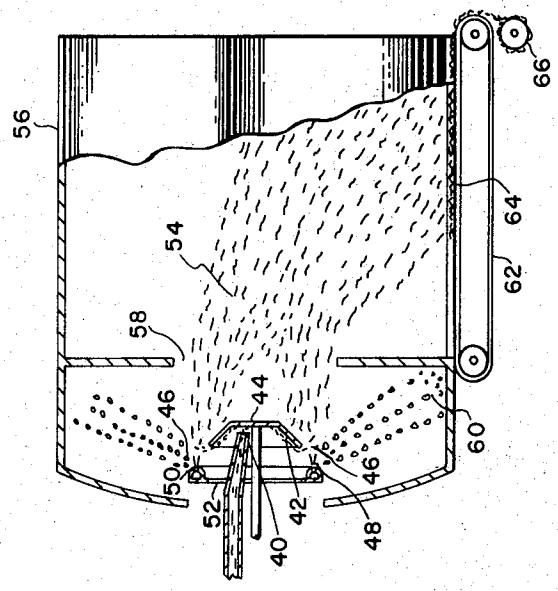
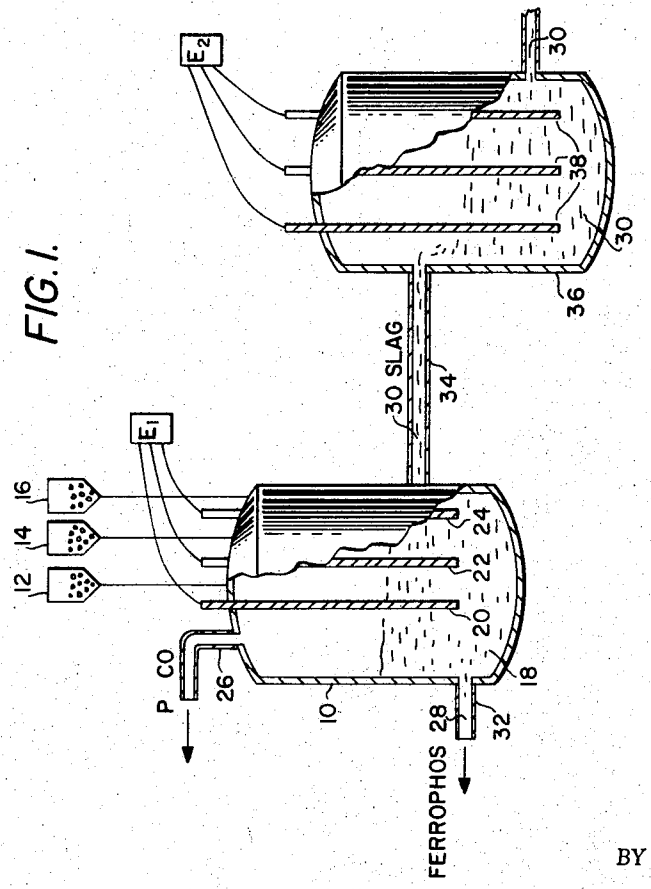



FIG. 1.




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# METHOD OF PREPARING FIBERS FROM BY-PRODUCT SLAG OF A PHOSPHORUS FURNACE

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2 Claims. (Cl. 264—8)

This invention relates to the manufacture of fibers from phosphorus-furnace slag, and particularly to the production of such fibers by a process which provides a high quality, stable product.

In our co-pending application, Ser. No. 481,973, filed Aug. 23, 1965 and entitled Method of Preparing Fibers From Solidified Phosphorus-Furnace Slag. We described the problems associated with production of fibers from phosphorus-furnace slags, and a method of overcoming these problems. It is discussed there how slags produced from phosphorus furnaces, typically from western U.S. and Florida phosphate slags, do not behave the same as typical steel furnace slags in fiber production.

Phosphorus furnace slags form fibers having a tendency toward physical weakness and physical degradation on aging, if they are produced by the obvious method of heating the slag to melt it and provide a slag melt viscosity of about 15 poises at which it can be used readily in typical fiber-forming processes by spinning streams of molten slag from a wheel and blowing these streams into fibers. Our aforementioned co-pending patent application describes our novel method of overcoming these problems by conditioning the slag prior to forming fibers from it by heating it to a conditioning temperature of at least 100° C. above the temperature at which it melts and has a suitable fiber-forming viscosity of 15 poises, for at least about 10 minutes. At this conditioning temperature it has a viscosity of 7 or less.

The described process is highly useful in making possible the production of useful and stable fibers from the plentiful and low-cost phosphorus furnace slags, by a process involving spinning streams of slag from a spinner wheel and attenuating these streams of slag into fibers with a flow of a gas. However, it necessitates providing a large amount of heat to the slag in order to melt it and to raise it to its conditioning temperature, and to maintain it there during the conditioning period.

It accordingly has remained desirable, and it is an object of this invention, to improve upon our aforesaid phosphorus-furnace slag conditioning process by simplifying the manner of operating, while at the same time making it possible to produce fibers from such slag in useful and stable form.

We have now found that we can achieve the desired end of producing from phosphorus-furnace slag, initially strong fibers which are resistant to physical degradation on aging, by feeding the slag removed from a phosphorus furnace while it is still in a molten condition to a fiber forming process which employs a slag spinner wheel and a gaseous attenuation means, provided the slag is not cooled to a temperature below that at which it is more viscous than 7 poises before being so fed.

In our process, a phosphate-containing ore composed generally of 22 to 26% $P_2O_5$, 29 to 43% CaO, 10 to 30% $SiO_2$ and the balance minor constituents such as about 3 to 10% $Al_2O_3$, 0.5 to 2% $Fe_2O_3$, moisture and other oxides, a source of $SiO_2$ and coke, are fed to an electric arc furnace in relative amounts to provide a rough weight ratio of $SiO_2$ to CaO of 0.75 to 1.05 parts of $SiO_2$:1 part of CaO. The coke is used in the amount of 1 to 1.1 parts per part of $P_2O_5$ and the transition metals present



and calculated as their oxides. This charge is heated electrically to 1350° to 1600° C. to provide a molten furnace burden and phosphorus vapor, the phosphorus vapor together with by-product carbon monoxide is taken off overhead from the furnace, and molten ferrophos and molten slag are recovered at a temperature of at least 2500° F. from the furnace burden.

The slag is composed largely of $CaSiO_3$, and typically contains 40 to 50% $SiO_2$, 45 to 50% CaO and the balance minor constituents such as 0.1 to 3% $P_2O_5$, 3 to 10% $Al_2O_3$ 0.1 to 1% $Fe_2O_3$, 1 to 3% F and the like metal oxides derived from the ore. We produce fibers from the slag by feeding it in its still molten form to a slag-spinner wheel at a temperature such that on the wheel it has a temperature of 1240° to 1450° C., and a viscosity of 0.5 to 7 poises. The molten slag is thrown off the slag-spinner wheel as streams of molten slag, the streams of molten slag so produced are blown or attenuated into fibers with a high velocity flow of gaseous fluid which may be jets of steam or air, and the fibers are collected.

Operation by our improved method permits highly economical production of physically sound and strong fibers which are resistant to physical degradation on aging, by the preferred fiber spinning and attenuating method and from typical phosphorus furnace slags.

It is important to realize that by employing unsolidified molten slag from the furnace we are able to avoid the possible formation of crystal nuclei or other solids deleterious to fiber formation; we believe such solids remain in phosphorus furnace slags which have been solidified and remelted at that temperature which provides a spinnable viscosity of 15 poises in the slag. This theory is advanced in our aforesaid co-pending patent application as a possible explanation of why our process as described therein is effective, and is equally applicable in explaining the effectiveness of our present improved process. Regardless of the correctness of this explanation, however, our process of employing molten phosphorus furnace slag without solidification and in which the slag temperature is held above that temperature which provides a slag viscosity of no more than about 7 poises until being spun from the slag-spinner wheel in the fiber-forming process, is extremely effective and productive of high quality stable fiber products.

In the attached drawings:

FIG. 1 is a schematic side view, partly cut away, of a phosphorus furnace and molten slag hold tank in operation; and

FIG. 2 is a schematic side view, also partly cut away, of a typical fiber forming apparatus.

Referring to the drawings, in FIG. 1 an electric reduction furnace **10** is shown receiving ore, silica and coke from hoppers **12**, **14** and **16** respectively. The reaction mixture or burden **18** in the furnace is kept in molten condition by electrodes **20**, **22** and **24** operating as a 3-phase system from electrical source $E_1$. The furnaces used operate at from 20 to 50 megawatts of power input. Other electrode systems obviously may be used in place of the three electrode system shown.

Elemental phosphorus vapor produced in the furnace is removed overhead via line **26** together with carbon monoxide by-product, and molten ferrophos **28** which is heavier than slag **30** settles and is removed via line **32** from the furnace.

Slag **30** is tapped from the furnace as a melt at a temperature on the order of about 2500° F. or higher and fed via line **34** to hold tank **36** equipped with heaters **38** powered by electrical source $E_2$ which maintain the molten slag at the herein required temperature.

From the hold tank, which may be dispensed with if

the slag is to be fed directly from the furnace **10** via a line **40** to the spinning operation, the molten slag is poured onto the side or upstanding face **42** of spinning wheel **44** from which it is thrown peripherally as streams **46** of molten slag. These streams **46** of slag are blown into fibers with air or steam blown across them as jets **48** emanating from holes **50** in ring **52** spaced slightly outside the periphery of the wheel **44**, and in front of its slag-receiving, upstanding face **42**.

The fibers **54** which are formed by the attenuating jets **48** of air or steam are collected in chamber **56** having a portal opening **58**. This opening is designed so as to permit separation of shot particles **60** from the stream of lighter fibers. Heavier shot drops out of the stream and only the fiber goes through opening **58** and into the collection chamber. Moving belt **62** beneath the chamber collects the fibers as loose matt **64**, which is collected on roll **66**.

The ores used in our process are mined principally in the western United States and Florida, although similar ores are found in other parts of the world. They normally contain 22 to 26% $P_2O_5$, 29 to 43% CaO, 10 to 30% $SiO_2$ and the balance minor constituents such as about 3 to 10% $Al_2O_3$, 0.5 to 2% $Fe_2O_3$, moisture and other oxides. The ore is best fed to the electric furnace as pellets having an average size of about ¼ to 3 inches in diameter. Such pellets are normally calcined in conventional fashion 2250° to 2500° F. in a rotary kiln, on a grate calciner or the like before being used in manufacture of phosphorus.

The $SiO_2$ ordinarily is obtained as quartz sand, and is used to provide a weight ratio of $SiO_2$ to CaO in the feed to the electric furnace of 0.75 to 1.05 parts of $SiO_2$:1 part of CaO. This ingredient is best fed in the form of pebbles, on the order of at least ¼ inch in diameter.

The coke also normally is fed as pieces having a size of at least 80% greater than ¼ inch in diameter. It is not essential that coke itself be used, it being possible to employ other reducing carbonaceous fuels, primarily coal, and when coke is referred to herein it is intended that these equivalent materials be included. The coke is used in an amount of 1 to 1.1 parts per part of $P_2O_5$ and the transition metals calculated as oxides. It serves both as an electrical conductor between the electrodes of the furnace, which operates at about 1350° to 1600° C., and as a reductant for $P_2O_5$. The reaction yields elemental phosphorus and carbon monoxide which are removed as gases.

The reaction in the furnace leaves behind both a molten composition known as ferrophos, composed of 55 to 60% Fe, 20 to 28% P, 4 to 5% V, 4% Cr, and other minor constituents, and a slag which is largely $CaSiO_3$. The slag is composed of 40 to 50% $SiO_2$, 45 to 50% CaO, 0.1 to 3% $P_2O_5$ and other minor constituents such as 0.1 to 3% $P_2O_5$, 3 to 10% $Al_2O_3$, 0.1 to 1% $Fe_2O_3$ and 1 to 3% F.

The ferrophos is heavier than the slag and is removed from the very bottom of the furnace. The slag is also tapped, from a point intermediate in the furnace, at a temperature of at least about 2500° F.

The slag removed from the furnace can either be fed directly at a proper fiber process temperature which provides a slag viscosity of about 7 poises or less to the fiber-forming process, or it can be held in a hold tank properly fitted with heaters to maintain it at a proper temperature for an indefinite period before being used in making fibers.

The temperature at which the slag is held is such as to retain it in a molten condition, and to avoid cooling it below a temperature at which it will have a viscosity of 7 poises or more on the face of the spinner wheel from which it is spun, allowing for heat losses which may occur during feeding and on the spinner. Failure to observe these requirements often results in provision of a slag which must be heated to its conditioning temperature for a conditioning time (as described in our aforesaid copending patent application Ser. No. 481,973) if it is to produce good quality age-resistant fibers. This manner of operating, of course, loses the economic and control advantages of our present process in which it is not necessary to supply large amounts of heat (additional to furnace heat) to the slag in order to produce fibers from it. The herein conditions apply only to operations in which the slag is spun on a slag-spinner wheel to form streams of slag, and then streams are attenuated into fibers with a high velocity flow of a gaseous fluid. Other methods operate under different conditions.

Formation of fibers from our slag is carried out by conventional means, employing a slag-spinner wheel to spin streams of molten slag and attenuating these slag streams into fiber with a high velocity gaseous fluid, for example by the methods taught in U.S. Patents 2,328,714; 2,646,593; 2,793,395 and the like. In a typical fiber producing process, the molten slag is fed either onto the face or onto the periphery of a dish-shaped, cupped or grooved wheel which spins at a speed of on the order of 700 to 2500 r.p.m. Typical wheels have a diameter of about 5 to 20 inches, although larger or smaller wheels may be useful in specific cases. The molten slag is spun off the wheel and the streams or possibly fibers, all referred to herein as streams, of molten slag thus discharged are blown into fibers by a high velocity gaseous fluid, such as steam or air in the form of jets to attenuate the slag into fibers. The fibers are collected by any of a variety of means, for example on a moving belt, in a hopper or in an aqueous or other liquid medium.

The following examples are presented by way of illustration of this invention only, and are not to be considered as limiting the scope thereof in any way. Temperatures given in the examples and throughout the specification and the appended claims are those determined with an optical pyrometer. They are about 60° C. lower than the internal temperature of the molten slag when measured with expendable thermocouples inserted into the slag.

*Example 1.—Production of slag*

Thirty-three and one-half tons per hour of a western phosphate shale containing 24% $P_2O_5$, 33% CaO, 28% $SiO_2$, 1% $Fe_2O_3$, 4% $Al_2O_3$, 1% MgO and 9% moisture, 2.9 tons per hour of quartz sand and 2.7 tons per hour of coke all as pellets having an average diameter of about ¼ to 2½ inches, were fed continuously into a 50 megawatt three-phase electric submerged arc furnace having three electrodes and operated at 50 megawatts.

Phosphorus vapor and carbon monoxide were continuously removed overhead and the phosphorus recovered under water. Ferrophos was continuously tapped from a side hole near the bottom of the furnace, and molten slag having a composition of 44.4% $SiO_2$, 46.6% CaO, 4.6% $Al_2O_3$, 0.84% $Fe_2O_3$, 0.96% MgO, 1.5% $P_2O_5$ and 1.1% F was removed continuously from a tap hole in the furnace above the level of the ferrophos which sank below the slag. The slag was recovered in the amount of 27 tons per hour, and was at a temperature of about 2500° to 2800° F. as it left the furnace.

*Example 2.—Production of fibers*

The molten slag removed from the electric furnace as described in Example 1 at a temperature of 2500° to 2800° F. was fed into a hold tank equipped with electric heaters, and maintained therein at a temperature of 1300° to 1400° C., which is sufficient to keep the material in molten condition and within its range of fiber-forming viscosities, namely 0.5 to 7 poises. It was fed from the hold tank after an average of 5 hours in the tank and at a temperature of 1350° C. to the upstanding face of a vertically positioned wheel having a disc-like face and having a diameter of 14 inches, spinning at 1400 r.p.m. This wheel was cooled by water pumped through channels within it and the slag on the wheel was at 1250° C.

The slag which was thrown outwardly from the edge of the wheel was blown by jets of steam at a pressure of 105 p.s.i.g. delivered from holes in a ring slightly outside the

periphery of the wheel and slightly in front of and facing the slag receiving side of the wheel to provide fibers which are collected on a moving belt behind which a suction device was positioned.

The fibers produced thereby were collected as a very loose mat on an endless collecting belt. They were then bagged. They were tested for slurry stability immediately upon being produced and cooled, and after storage for 3 months. In both cases the properties were essentially the same, with the slurry stability initially being 270 ml., and after 3 months storage being 262 ml. Slurry stabilities are determined by agitating a 25 gram sample of wool in 500 ml. of water (70° F.±5°) for 20 seconds in a 15,000 r.p.m. Waring Blendor equipped with case hardened blades. The slurry is quickly transferred to a 1000 ml. graduated cylinder and the height in ml. of the settling wool column is recorded after 5 minutes. A wool column 250 ml. or greater is indicative of a material that should run well in wet-processing, e.g., board manufacture. Fibers having a slurry stability of about 225 ml. or more are adequate for insulation and other dry fiber uses.

*Example A.—Comparative*

The process of Example 2 was followed with the exception that the heaters in the hold tank were not turned on with the result that the temperature of the slag dropped to 1220° C., and the viscosity was 8 poises. It was then fed to the wheel where it had a temperature of 1130° C. Fibers produced thereby had a slurry stability initially (on removal from the fiber-forming process) of 170 ml. and a slurry stability after 3 months of about 140 ml.

Pursuant to the requirement of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that within the scope of the appended claims the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:



**1.** The method of producing mineral fibers while producing elemental phosphorus and ferrophos from phosphorus-containing shale composed generally of 22 to 26% $P_2O_5$, 29 to 43% CaO, 10 to 30% $SiO_2$, and the balance minor constituents including 3 to 10% $Al_2O_3$, 0.5 to 2% $Fe_2O_3$ and moisture, an $SiO_2$ source and coke, comprising feeding to an electric arc furnace a charge composed of said shale, said $SiO_2$ source and said coke in relative amounts to provide a weight ratio of $SiO_2$ to CaO of 0.75 to 1.05 parts of $SiO_2$:1 part of CaO, and 1 to 1.1 parts of coke per part of $P_2O_5$ and transition metals calculated as their oxides, electrically heating said charge in said electric arc furnace to 1350° to 1600° C. to provide a molten furnace burden and phosphorus and carbon monoxide vapors, removing said phosphorus and carbon monoxide from said furnace, separately recovering ferrophos and a molten slag at a temperature of at least 2500° F. from furnace burden, said slag being composed substantially of 40 to 50% $SiO_2$, 45 to 50% CaO, 0.1 to 3% $P_2O_5$, 3 to 10% $Al_2O_3$, 0.1 to 1% $Fe_2O_3$, 1 to 3% F and other minor constituents, and producing fibers from said molten slag by feeding the slag in molten form to a slag-spinner wheel while said molten slag is at a temperature of 1240° to 1450° C. and a viscosity of not greater than 7 poises and is maintained in a molten condition and at a temperature such that it is not cooled to a temperature at which it has a viscosity higher than 7 poises on a said slag-spinner wheel, whereby the wheel discharges streams of molten slag outwardly from said wheel, and intercepting said streams by a high velocity flow of a gaseous fluid to attenuate the streams into fibers.

**2.** The method of claim **1** in which the viscosity of the molten slag on the slag-spinner wheel is 0.5 to 7 poises.

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